An apparatus proposed for density measurements in compressed liquid regions at pressures of 0.1–60 MPa and temperatures of 288.15–413.15 K

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(Received 27 November 2014, revised 16 March, accepted 17 March 2015)

Abstract: In this work, an apparatus for density measurements in the compressed liquid regions is presented. This installation is based on the use of a DMA HP density measuring cell and a DMA 5000 densimeter (both instruments are products of Anton Paar, Gratz, Austria). Calibration of the DMA HP cell was performed by applying the classical method in which a vacuum, water and \( n \)-decane were recommended to be used as calibration fluids. To test the capabilities of the set-up, the densities of \( n \)-hexane, toluene and dichloromethane were measured in the temperature interval 288.15 to 413.15 K and the pressure range 0.1–60 MPa. The obtained results were compared with the corresponding values found in the literature. Depending on the literature selected for comparison (the temperature and pressure ranges available), the average absolute percentage deviations were for \( n \)-hexane, 0.03–0.10 %; for toluene, 0.04–0.08 % and for dichloromethane, 0.02–0.03 %. A deeper insight into the results of this work showed that most of them were in good agreement with the literature values; higher discrepancies were evidenced in the vicinity of the ends of the temperature and pressure ranges.

Keywords: high pressure; elevated temperature; density; \( n \)-hexane; toluene; dichloromethane.

INTRODUCTION

It is well known that density represents one of the most important properties of fluids, from both the theoretical and practical points of view.

Namely, accurate density data can help to clarify molecular structure of pure liquid substances and of their mixtures at defined temperatures, pressures and composition. Some essential liquid properties that can be derived from density
measurements are thermomechanical coefficients, such as the isothermal compressibility, $\kappa_T$, and the isobaric thermal expansion coefficient, $\alpha_p$. Based on these properties, the internal pressure, important for studying attractive and repulsive forces present in liquids, can also be determined. By coupling the mentioned isothermal and isobaric properties, $\kappa_T$ and $\alpha_p$, and by using the isentropic compressibility $\kappa_S$ (that is related to the thermodynamic speed of sound), some additional properties can be calculated; in this respect, the isobaric heat capacity and the difference in the isobaric and isothermal heat capacity ($C_p - C_V$) could be mentioned.

From the practical point of view, density data are of utmost importance in the development of new and the testing of existing equations of state; these equations have significant value in the design and operation of production plants in chemical and related process industries.

In our group, over a longer period, some important physical/thermodynamic and transport properties have been investigated; the obtained results were correlated and several modern prediction methods were tested. Mostly, pure non-electrolyte substances and mixtures were investigated, although systems with ionic liquids were also included.$^{1-5}$ These activities were performed under ambient pressure and in the temperature range up to 333.15 K.

In this work, the results of an effort to extend the research to the conditions of elevated temperatures and high pressures are presented. In this respect, the proposed apparatus, based on the principle given by Gardas et al.,$^6$ was developed and constructed. The classical method of Lagurette et al.,$^7$ that was recently adjusted by Comuñas et al.$^8$ for use in broad ranges of temperature and pressure, was chosen for calibration. A vacuum and water were used as calibration fluids, except under conditions where water was no longer in liquid state, when the calibration fluids were vacuum and $n$-decane. The proposed set-up was tested using $n$-hexane, since it was suggested as a model substance for compressed simple liquids.$^9-12$ In addition, toluene and dichloromethane were also selected for testing the employed device and the experimental procedure followed.

**EXPERIMENTAL**

**Materials**

$n$-Hexane, $n$-decane and toluene were purchased from Merck with purities of $\geq 99.0$, $\geq 99$ and $\geq 99.9$ mass %, respectively. Sigma–Aldrich supplied dichloromethane with a purity of $\geq 99.9$ mass %.

The purities of the used substances were checked by comparing their measured densities at atmospheric pressure and at various temperatures with the corresponding literature values (Table S-I of the Supplementary material to this paper) and they were in a good agreement, within 0.2, 0.5 and 0.7 kg m$^{-3}$ for $n$-hexane, toluene and dichloromethane, respectively.

Nitrogen 5.0 was provided by Messer Tehnogas, AD, with a purity of $>99.999$ mass %.
The double deionized Millipore water, provided by Veolia IonPRO-LX MkII system, was used as a calibration fluid. The treated water has a specific conductivity of 2.5 µS cm\(^{-1}\) and a specific resistance of 18 MΩ cm.

**Apparatus – Description of the set-up**

The compressed liquid densities at various temperatures and pressures were experimentally studied, employing an Anton Paar DMA HP density-measuring cell for high pressures and temperatures, connected to an Anton Paar DMA 5000 vibrating tube densimeter, as shown schematically in Fig. 1.

As mentioned in the introductory section, the proposed apparatus has been based on the principle proposed by Gardas et al.,\(^6\) although some additional parts of equipment have been brought into the system to construct the set-up.

The apparatus was used in broad ranges of temperature and pressure, varying between 288.15–413.15 K and 0.1–60 MPa, respectively. Each selected temperature was controlled with an integrated Peltier thermostat and the expanded uncertainty (coverage factor \(k = 2\)) for the temperature was 0.01 K.

A pressure generator, model 50-6-15, from High Pressure Equipment Co. (HiP), was used to adjust and control the pressure in the system; acetone was used as a hydraulic fluid, as proposed in the literature.\(^6\) The pressure in the system was measured using a pressure transducer WIKA, S-10, Alexander Wiegand GmbH & Co. The transducer was calibrated up to 60 MPa and the expanded uncertainty (\(k = 2\)) for the pressure was 0.05 MPa.

The period of tube vibration, \(\tau\) was read on the display of the DMA 5000 densimeter with a digital counter; the vibrating period was displayed to seven significant digits.

All tubing (1/16" and 1/8" O.D.), the high-pressure valves and other high-pressure fittings shown in Fig. 1 are products of HiP Co, USA.

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A syringe pump, enabling precise flow control during charging of the sample fluid, was used in order to avoid the formation of micro-bubbles in the capillary tube of the densimeter.

The assembly presented in Fig. 1 incorporates additional pieces of equipment, some of them are mentioned here: the DuoSeal vacuum pump, Welch model 1400, capable to reach an ultimate vacuum down to ca. 0.133 Pa (0.001 torr); the vacuum was indicated by a Pirani–Penning instrument; a KGW Isotherm cold trap was situated near the entrance of the pump; in addition, a compressed nitrogen bottle was included in the installation. The stainless steel spiral buffer tube (1/16" O.D. and ca. 1.5 m long) guarantees the absence of diffusion of the hydraulic liquid contained in the densimeter cell.

Transferring of the collected data (period of oscillation of U-tube, cell temperature and pressure) from the DMA HP to the DMA 5000 was enabled by connecting the S-BUS interface of the DMA HP and DMA 5000.

The APSofPrint software program (a Microsoft Excel Add-In) was employed to read out and transfer the measured values to a PC.

**Loading of the set-up with the pressurizing fluid**

To prepare the apparatus for experimental runs, the pressurizing fluid should be introduced into the appropriate parts: the tubes (and fittings), connecting valves V2 through V5 (Fig. 1), and those that join the high-pressure generator (HPG) with the pressure transducer. The HPG must also be filled.

To remove air from the parts of the installation described, the valves V3 and V5 are opened, enabling access to the vacuum pump (valve V2 is closed). After several hours of evacuation, valve V5 is closed. Then, a Hamilton multilayer silicon rubber septum, being a part of the pressurizing fluid reservoir (not shown in detail in Fig. 1), is penetrated by a needle of a syringe containing degassed acetone. In this way, acetone will occupy the entire evacuated space.

**The measurement procedure**

Before starting any run, the part of circuit between the syringe pump and valve V2 (V2 and V4 were closed) was cleaned by successive use of ethanol and acetone to remove residues from the previous sample; then dry nitrogen gas was circulated through this part of the system for an appropriate period.

After a slight release of the connection between the buffer tube and the entrance of the valve V2/V4, the syringe pump was started, dispensing the sample between the valves V1 and V2, until several drops of the fluid had been withdrawn from the apparatus; then the pump was stopped and the mentioned connection tightened again. Since the tubes between the valves V1 and V2 were filled with the sample, the valve V1 was closed. Hence, the sample was introduced into the system by the described operation. Now, when the desired conditions of temperature and pressure in the cell were stable, the vibration period of the U-tube could be determined.

In the present work, isothermal measurements were performed; at each selected isotherm, the pressure was imposed starting from its initial (lowest) value and elevating it towards the maximum value. Hysteresis effects were checked at every isotherm. Then, the temperature of the cell was changed and measurements at a new isotherm were performed.

**Calibration**

Since the vibrating tube densimeter does not generate directly the density values, it is necessary to calculate the density from the measured period of the oscillation (under a defined temperature $T$ and pressure $p$).
Based on the model of the performance of vibrating tube established by Kratky et al., the period of vibration $\tau(T,p)$ can be related to the sample density $\rho(T,p)$ by a linear function that incorporates two apparatus parameters $A(T,p)$ and $B(T,p)$:

$$\rho(T,p) = A(T,p)\tau^2(T,p) - B(T,p)$$  \hspace{1cm} (1)

According to the approach of Lagourette et al., who hypothetically assumed that the parameter $A$ depends only on temperature while the parameter $B$ remains dependent upon both temperature and pressure, Eq. (1) could be rewritten in the form:

$$\rho(T,p) = A(T)\tau^2(T,p) - B(T,p)$$  \hspace{1cm} (2)

Use of this equation considerably simplifies the calibration of the densimeter (i.e., the determination of its parameters $A(T)$ and $B(T,p)$). This method has to be performed by measuring the oscillating period of the evacuated tube over the entire temperature range of interest. In addition, the period of the tube full of the chosen reference fluid, having the certified density, has to be measured over the entire temperature and pressure ranges of the experimental significance. Lagourette et al. performed the calibration using the accurate density values for water of Kell and Whalley in the temperature and pressure ranges 293.15–373.15 K and 0.1–40 MPa, respectively.

Comuñas et al. adjusted the calibration procedure of Lagourette et al. in order to make it suitable for the new equipment (Anton Paar DMA HPM), enabling measurements in broad ranges of temperature and pressures up to 403.15 K and up to 140 MPa, respectively.

Thus, the procedure of Comuñas et al. was employed to calibrate the Anton Paar DMA HP densimeter included in Fig. 1.

For the specific volume of water, Fisher and Dial selected the Tumlirz equation in the form given in the analysis of Eckert:

$$V_p = V_\infty + \frac{\lambda}{p_0 + p}$$  \hspace{1cm} (3)

where $V_p$, cm$^3$ g$^{-1}$ is the specific volume as a function of pressure and temperature; $V_\infty$, cm$^3$ g$^{-1}$, $\lambda$, bar cm$^3$ g$^{-1}$ and $p_0$, bar, are the pure water parameters. For these parameters, analytical functions were obtained that, in conjunction with Eq. (3), accurately represent the high precision data of Kell and Whalley (within 8 ppm from 273.15–373.15 K and within 15 ppm from 373.15–423.15 K, up to 100 MPa):

$$V_\infty = 0.6980547 - 0.7435626 \times 10^{-3} T + 0.3704258 \times 10^{-4} T^2 - 0.6315724 \times 10^{-6} T^3 + 0.9829576 \times 10^{-8} T^4 - 0.1197269 \times 10^{-10} T^5 + 0.3457898 \times 10^{-12} T^6 - 0.5437898 \times 10^{-14} T^7 + 0.169946 \times 10^{-16} T^8 - 0.2295063 \times 10^{-19} T^9$$  \hspace{1cm} (4)

$$\lambda = 1788.316 + 21.55053 T - 0.4695911 T^2 + 3.096363 \times 10^{-3} T^3 - 0.7341182 \times 10^{-5} T^4$$  \hspace{1cm} (5)

$$p_0 = 5918.499 + 58.05267 T - 1.1253317 T^2 + 6.6123869 \times 10^{-3} T^3 - 1.4661625 \times 10^{-5} T^4$$  \hspace{1cm} (6)

Finally, the specific volume values for water, supplied in this way, were recalculated to density. Accordingly:

a) at $0.1 \leq p \leq 60$ MPa and $288.15 \leq T \leq 363.15$ K, calibration of the cell was realized using the data collected as described above and by employing the following equation:

$$\rho_p = \frac{V_p}{V_\infty}$$  \hspace{1cm} (7)

Where the following values were used:

$$V_\infty = 0.6980547 - 0.7435626 \times 10^{-3} T + 0.3704258 \times 10^{-4} T^2 - 0.6315724 \times 10^{-6} T^3 + 0.9829576 \times 10^{-8} T^4 - 0.1197269 \times 10^{-10} T^5 + 0.3457898 \times 10^{-12} T^6 - 0.5437898 \times 10^{-14} T^7 + 0.169946 \times 10^{-16} T^8 - 0.2295063 \times 10^{-19} T^9$$  \hspace{1cm} (4)

$$\lambda = 1788.316 + 21.55053 T - 0.4695911 T^2 + 3.096363 \times 10^{-3} T^3 - 0.7341182 \times 10^{-5} T^4$$  \hspace{1cm} (5)

$$p_0 = 5918.499 + 58.05267 T - 1.1253317 T^2 + 6.6123869 \times 10^{-3} T^3 - 1.4661625 \times 10^{-5} T^4$$  \hspace{1cm} (6)
\[ \rho(T, p) = \rho_{\text{water}}(T, p) + \rho_{\text{water}}(T, 0.1 \text{ MPa}) \left[ \frac{\tau^2(T, p) - \tau^2_{\text{water}}(T, p)}{\tau^2_{\text{water}}(T, 0.1 \text{ MPa}) - \tau^2_{\text{vacuum}}(T)} \right] \]  

(7)

Here, \( \rho_{\text{water}}(T, p) \) is the density of water at \( T \) and \( p \); \( \rho_{\text{water}}(T, p) \) represents the period of the oscillation of the vibrating tube full of water at \( T \) and \( p \); \( \tau_{\text{vacuum}}(T) \) stands for the period of the evacuated tube at temperature \( T \).

b) At \( p = 0.1 \text{ MPa} \) and \( T \geq 373.15 \text{ K} \): under these conditions, water is no longer appropriate to be employed as the reference fluid because it exists in the gaseous state. In the present work, \( n \)-decane was used, as proposed by Comuñas et al.\(^8\) Hence, the data given in the literature\(^18\) was employed; under these circumstances, the following relation was used instead of Eq. (7), as shown in reference:\(^8\)

\[ \rho(T, 0.1 \text{ MPa}) = \rho_{n\text{-decane}}(T, 0.1 \text{ MPa}) \left[ 1 + \frac{\tau^2(T, 0.1 \text{ MPa}) - \tau^2_{n\text{-decane}}(T, 0.1 \text{ MPa})}{\tau^2_{n\text{-decane}}(T, 0.1 \text{ MPa}) - \tau^2_{\text{vacuum}}(T)} \right] \]  

(8)

c) At \( p > 0.1 \text{ MPa} \) and \( T \geq 373.15 \text{ K} \), Eq. (9) given by Comuñas et al.\(^8\) was used in the present work:

\[ \rho(T, p) = \rho_{\text{water}}(T, p) + \rho_{n\text{-decane}}(T, 0.1 \text{ MPa}) \left[ \frac{\tau^2(T, p) - \tau^2_{\text{water}}(T, p)}{\tau^2_{n\text{-decane}}(T, 0.1 \text{ MPa}) - \tau^2_{\text{vacuum}}(T)} \right] \]  

(9)

By employing the described calibration procedure in the temperature and pressure ranges of interest (288.15–413.15 K and 0.1–60 MPa, respectively), numerous measurements, distributed on 16 isotherms were performed.

The parameters \( A(T) \) and \( B(T, p) \) of Eq. (2) were determined using Eqs. (10) and (11), respectively, which were clearly presented in the explicit form by Segovia et al.\(^19\):

\[ A(T) = \frac{\rho_{\text{ref1}}(T, 0.1 \text{ MPa})}{\tau^2_{\text{ref1}}(T, 0.1 \text{ MPa}) - \tau^2_{\text{vacuum}}(T)} \]  

(10)

\[ B(T, p) = \rho_{\text{ref1}}(T, 0.1 \text{ MPa}) \frac{\tau^2_{\text{ref1}}(T, p)}{\tau^2_{\text{ref1}}(T, 0.1 \text{ MPa}) - \tau^2_{\text{vacuum}}(T)} - \rho_{\text{ref2}}(T, p) \]  

(11)

where \( \rho_{\text{ref1}} \) and \( \rho_{\text{ref2}} \) are the densities of reference fluids 1 and 2, respectively, and \( \tau_{\text{ref1}} \) and \( \tau_{\text{ref2}} \) are the oscillation period of the U tube full of reference fluid 1 and 2, respectively. For the interval: \( 0.1 \leq p \leq 60 \text{ MPa} \) and \( 288.15 \leq T \leq 363.15 \text{ K} \), both reference fluids are water. At \( p = 0.1 \text{ MPa} \) and \( T \geq 373.15 \text{ K} \), ref1 and ref2 refer to \( n \)-decane and at \( p > 0.1 \text{ MPa} \) and \( T \geq 373.15 \text{ K} \), reference fluid 1 is \( n \)-decane while reference fluid 2 is water.

As could be seen from Fig. 2a, the values of \( A(T) \) decreased linearly with increasing temperature, as expected according to the conclusions of Lagourette et al.\(^7\) In addition, these authors remarked that the ratio of the calibration parameters \( A(T)/B(T, p) \) is practically independent of pressure. This observation was appraised by a number of authors who employed various calibration fluid pairs.\(^19,21\) In each of these cases, it was shown that the ratio \( A(T)/B(T, p) \) decreased slightly with increasing pressure. The dependence of the ratio of the calibration parameters on pressure at the selected isotherms chosen in the present work is demonstrated in Fig. 2b.

The calculated expanded uncertainty of the density measurements with a coverage probability of 95 % (coverage factor \( k = 2 \)) is 1.7 kg m\(^{-3}\) in the temperature interval 288.15–363.15 K, and 2.7 kg m\(^{-3}\) at temperatures 373.15–413.15 K.
Fig. 2. The calibration parameters: a) dependence of $A(T)$ of the temperature, 288.15–413.15 K, b) the ratio of the $A(T)/B(T.p)$ vs. pressure at different temperatures: (■) 288.15, (○) 303.15, (▲) 318.15, (◇) 333.15, (●) 343.15, (★) 353.15, (▲) 363.15, (●) 373.15, (●) 393.15 and (△) 413.15 K.

The influence of viscosity of the substances on density was also studied. A personal correspondence with the supplier Anton Paar provided the information necessary for the calculation of density correction due to damping effects on the vibrating tube. Assuming that temperature has a greater impact on viscosity than pressure and that the viscosity decreases with increasing temperature, literature data22-24 for the viscosity at lower temperatures from the interval of interest in this work were used for the calculation. The calculated differences between the densities presented in this work and those corrected because of the viscosity effect for all three examined substances were under 0.03 kg m$^{-3}$, which was significantly lower than the calculated value of the expanded uncertainty for density and hence the viscosity influence on density were neglected.

RESULTS AND DISCUSSION

With the intention of checking the quality of the calibration parameters obtained in this study, the densities of $n$-hexane, toluene and dichloromethane, were experimentally determined and compared with some corresponding literature data.

The vibration periods of the U tube within the DMA HP densimeter full of samples, $n$-hexane, toluene or dichloromethane, were measured in the temperature range 288.15–413.15 K, at 16 isotherms, and at pressures up to 60 MPa. The densities of the measured substances were calculated by application of Eqs. (3)–(9) and the obtained values are presented in Tables S-II–IV of the Supplementary material to this paper.

The following criteria, the absolute average percentage deviation ($AAD$), the percentage maximum deviation ($MD$) and the average percentage deviation ($Bias$) were used to evaluate the quality of the agreement of the obtained experimental results with the corresponding literature values:
\[
AAD = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{\rho_i^{\text{exp}} - \rho_i^{\text{lit}}}{\rho_i^{\text{exp}}} \right| \]
(12)

\[
MD = \max \left( \frac{100}{N} \sum_{i=1}^{N} \left( \frac{\rho_i^{\text{exp}} - \rho_i^{\text{lit}}}{\rho_i^{\text{exp}}} \right) \right) ; i = 1,N
\]
(13)

\[
Bias = \frac{100}{N} \sum_{i=1}^{N} \left( \frac{\rho_i^{\text{exp}} - \rho_i^{\text{lit}}}{\rho_i^{\text{exp}}} \right)
\]
(14)

where \(N\) stands for the number of experimental points, \(\rho_{\text{exp}}\) denotes the experimental density and \(\rho_{\text{lit}}\) is the density value from the selected literature.

**n-Hexane**

The measured data for \(n\)-hexane (Table S-II) were compared with the densities given in the work of Troncoso *et al.*\(^{25}\) in the temperature range 288.15–313.15 K and at pressures up to 40 MPa. The comparison presented in Fig. 3a shows that the present measurements are in accordance with the tabulated data of Troncoso *et al.* \((AAD = 0.03 \% \text{ (less than 0.2 kg m}^{-3})\), \(MD = 0.09 \% \text{ and } Bias = -0.02 \%\). The agreement with the values of Daridon *et al.*\(^{26}\) is moderate in the presented region \((AAD = 0.08 \% \text{ (less than 0.6 kg m}^{-3})\), \(MD = 0.22 \% \text{ and } Bias = -0.08 \%\).

The obtained experimental results were compared with the tabulated data of Daridon *et al.*\(^{26}\) in the temperature interval 293.15–373.15 K and at pressures up
to 60 MPa. The calculated deviations were: $AAD = 0.10\ %$ (less than 0.7 kg m$^{-3}$), $MD = 0.29\ %$ and $Bias = -0.01\ %$, as shown in Fig. 3b.

In addition, the measurements were compared with the density data of Sanmamed et al.$^{27}$ in the regions: 288.15–323.15 K and up to 60 MPa. The obtained values of the criteria were: $AAD = 0.05\ %$ (less than 0.4 kg m$^{-3}$), $MD = 0.17\ %$ and $Bias = -0.04\ %$ that could be considered as acceptable.

In conclusion, the density measurements are in very good agreement with those of Troncoso et al.$^{25}$, as well as in accordance with those of Sanmamed et al.$^{27}$ On the other hand, the agreement with the tabulation of Daridon et al.$^{26}$ which were based on speed of sound measurements, are less good than expected, but should be emphasized that the densities reported in the literature$^{26}$ belong to a much wider temperature interval.

**Toluene**

The experimental densities of toluene, given in Table S-III, were compared with those obtained from the equations proposed by Cibulka and Takagi$^{28}$ over the entire temperature and pressure ranges of interest in the present work. The $AAD$ of the comparison was 0.04\ % (less than 0.3 kg m$^{-3}$), the $MD$ was 0.12\ % and the $Bias$ was $-0.04\ %$; hence, it could be concluded that the results obtained in the present study are in good agreement with those calculated by the procedure proposed in the literature.$^{28}$ This fact could be noticed by inspecting Fig. 4.

Density data of the present work were also compared with the data calculated from the fit given by Assael et al.$^{29}$ in the temperature range 288.15–373.15 K and up to 60 MPa. The values of the criteria for this comparison were: $AAD = 0.08\ %$ (less than 0.7 kg m$^{-3}$), $MD = 0.15\ %$ and $Bias = -0.08\ %$. It should be emphasized that the dispersion of the present data corresponded to that given in Fig. 2 of reference.$^{29}$

![Fig. 4. Comparison of the experimental densities with those obtained using the equation reported by Cibulka et al.$^{28}$ for toluene at various temperatures: (■) 288.15, (○) 303.15, (▲) 318.15, (▽) 333.15, (◆) 343.15, (★) 353.15, (★) 363.15, (□) 373.15, (●) 393.15 and (△) 413.15 K.](image-url)
In order to assess the obtained densities, an additional comparison was made. Namely, Segovia et al.\textsuperscript{19} gave a set of density data at various temperatures and pressures (288.15–393.15 K and up to 60 MPa). These data were fitted to the modified Tammann–Tait equation for comparison with the densities given in the present work:

\[ \rho = \frac{\rho_{\text{ref}}}{1 - C \ln \left( \frac{B(T) + p}{B(T) + p_{\text{ref}}} \right)} \]  \hspace{1cm} (15)

where \( \rho_{\text{ref}} \) is density at the reference pressure, \( p_{\text{ref}} \), which was chosen to be 0.1 MPa. The parameter \( C \) was treated as temperature independent and \( B(T) \) was obtained using the polynomial expression:

\[ B(T) = \sum_{i=0}^{2} b_i T^i \]  \hspace{1cm} (16)

The values of the individual criteria were: \( AAD = 0.05\% \) (less than 0.4 kg m\(^{-3}\)), \( MD = 0.09\% \) and \( \text{Bias} = -0.04\% \).

By reviewing the values of the criteria mentioned above, it could be noticed that the densities reported herein are in close agreement with the corresponding results appearing in the literature.

**Dichloromethane**

Gonçalves et al.\textsuperscript{22} presented a correlation for calculating the densities of dichloromethane in broad ranges of temperature and pressure that was used for comparison with the present data measured in the temperature interval 288.15–413.15 K and under pressures of up to 60 MPa (presented in Table S-IV). Deviations between these two density sets were: \( AAD = 0.03\% \) (less than 0.4 kg m\(^{-3}\)), \( MD = 0.13\% \) and \( \text{Bias} = -0.002\% \), indicating good agreement that is visible in Fig. 5.

In the work of Lugo et al.\textsuperscript{20} a density data set for dichloromethane was presented, covering temperature and pressure ranges of 293.15–353.15 K and 0.1–25 MPa. The present measurements were compared with the density values presented therein; the following deviations were reached: \( AAD = 0.03\% \) (less than 0.4 kg m\(^{-3}\)), \( MD = 0.04\% \) and \( \text{Bias} = -0.03\% \), showing good agreement between the two sets of data.

In addition, the densities of dichloromethane given by Demiriz\textsuperscript{30} in broad temperature and pressure ranges were employed to assess the densities from the present work. These data\textsuperscript{31} were fitted to the Tammann–Tait equation, according to Eqs. (15) and (16) and in this case \( p_{\text{ref}} \) was 1 MPa in the ranges: 270–430 K and up to 60 MPa. The densities obtained in the present work agreed quite well.
with those estimated using this fit. The deviations achieved were: \( AAD = 0.03 \% \) (less than 0.5 kg m\(^{-3}\)), \( MD = 0.30 \% \) and \( Bias = -0.03 \% \).

Values of the criteria given in this section could be considered as good and acceptable compared to those reported by the other authors.

![Fig. 5. Comparison of experimental densities with those obtained using the equation reported by Gonçalves et al.\(^{24}\) for dichloromethane at various temperatures: (■) 288.15, (○) 303.15, (▲) 318.15, (▼) 333.15, (●) 343.15, (△) 353.15, (◊) 363.15, (□) 373.15, (●) 393.15 and (△) 413.15 K.](image)

**CONCLUSIONS**

In this work, an apparatus proposed for compressed liquids density measurement over broad ranges of temperature and pressure was described. The Anton Paar DMA HP and Anton Paar 5000 represent the central parts of the set-up. This variable volume apparatus makes use of a buffer tube, as proposed by Gardas et al.\(^{6}\). The DMA HP was calibrated by applying the method of Comuñas et al.\(^{8}\) in the temperature and pressure ranges: 288.15 to 413.15 K and 0.1–60 MPa, respectively. The present density measurements for \( n \)-hexane, toluene and dichloromethane were compared with the corresponding literature values. This assessment showed good quality of the measurements performed. Thus, it could be expected that the recommended apparatus could be reliably applied for measuring the density of a number of other compressed liquids in broad ranges of temperatures and pressures.

**SUPPLEMENTARY MATERIAL**

The experimental values of the densities of \( n \)-hexane, toluene and dichloromethane at different temperatures (288.15–413.15 K) and pressures (0.1–60 MPa), as well as at atmospheric pressure, are available electronically from http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

**Acknowledgements.** It is our pleasure to thank Professor Abel Ferreira (Faculdade de Ciências e Tecnologia, Universidade de Coimbra, Portugal) for valuable discussion. Furthermore, we highly appreciate the Anton Paar GmbH, Graz, Austria for donating a DMA HP density-measuring cell to our laboratory, on the occasion of the fortieth anniversary of the vibrating tube densimeter invention. The authors gratefully acknowledge the financial support...
received from the Research Fund of Ministry of Education, Science and Technological Development of the Republic of Serbia (project No 172063) and the Faculty of Technology and Metallurgy, University of Belgrade.

ИЗВОД
АПАРАТУРА ПРЕДЛОЖЕНА ЗА МЕРЕЊЕ ГУСТИНА У ОБЛАСТИ КОМПРИМОВАНЕ ТЕНЧНОСТИ ОД 0,1 ДО 60 МПа И НА ТЕМПЕРАТУРАМА ОД 288,15 ДО 413,15 К

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У овом раду је предложена апаратура за мерење густине у области компримованих течности. Инсталација се заснива на коришћењу ћелије за мерење густине DMA НР и густиноомера DMA 5000 (производач оба производа је Anton Paar, Грац, Аустрија). Калибрacija ћелије DMA НР је извршена применом класичне методе која препоручује употребу вакуума, воде и n-декана као калибрационих флuida. У циљу провере рада причане апаратури мерење су густине n-хексана, толуена и дихлорметана у температурном интервалу 288,15 до 413,15 К и опсегу притиска од 0,1 до 60 МПа. Добијени резултати су упоређени са одговарајућим вредностима из литературе. У зависности од одабране литература, односно опсега температуре и притиска, добијена су следећи средњи апсолутна процентуална одступања: за n-хексан, 0,03–0,10 %; за толуен, 0,04–0,08 %, а за дихлорметан, 0,02–0,03 %. Детаљнији увид у результате овог рада показује да је већина их у доброј сагласности са вредностима из литературе; веће разлике су приметне у близини крајева интервала температуре и притиска.

(Примљено 27. новембра 2014, ревизирано 16. марта, прихваћено 17. марта 2015)

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